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(54) **CRYOGENIC RECTIFICATION SYSTEM FOR PRODUCING HIGH PURITY OXYGEN**

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(52) **U.S. Cl.** **62/652**; 62/654
(58) **Field of Search** 62/652, 654

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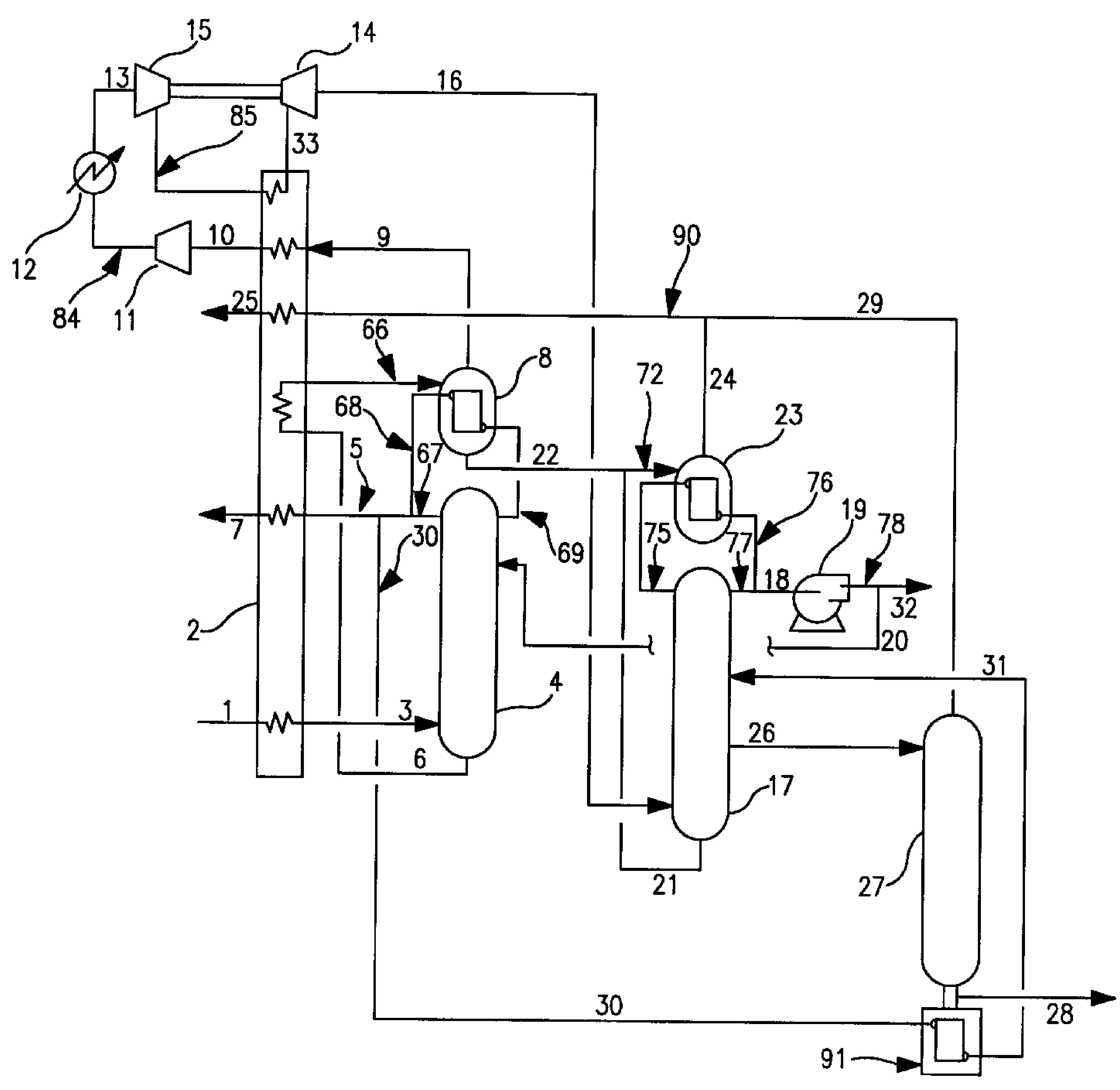
(57) **ABSTRACT**

A cryogenic rectification system comprising three columns wherein high purity oxygen is produced in the third column which is fed from at least one of the first and second columns, which do not share a common condenser/reboiler, and reboiled using feed air or first column top vapor.

19 Claims, 3 Drawing Sheets



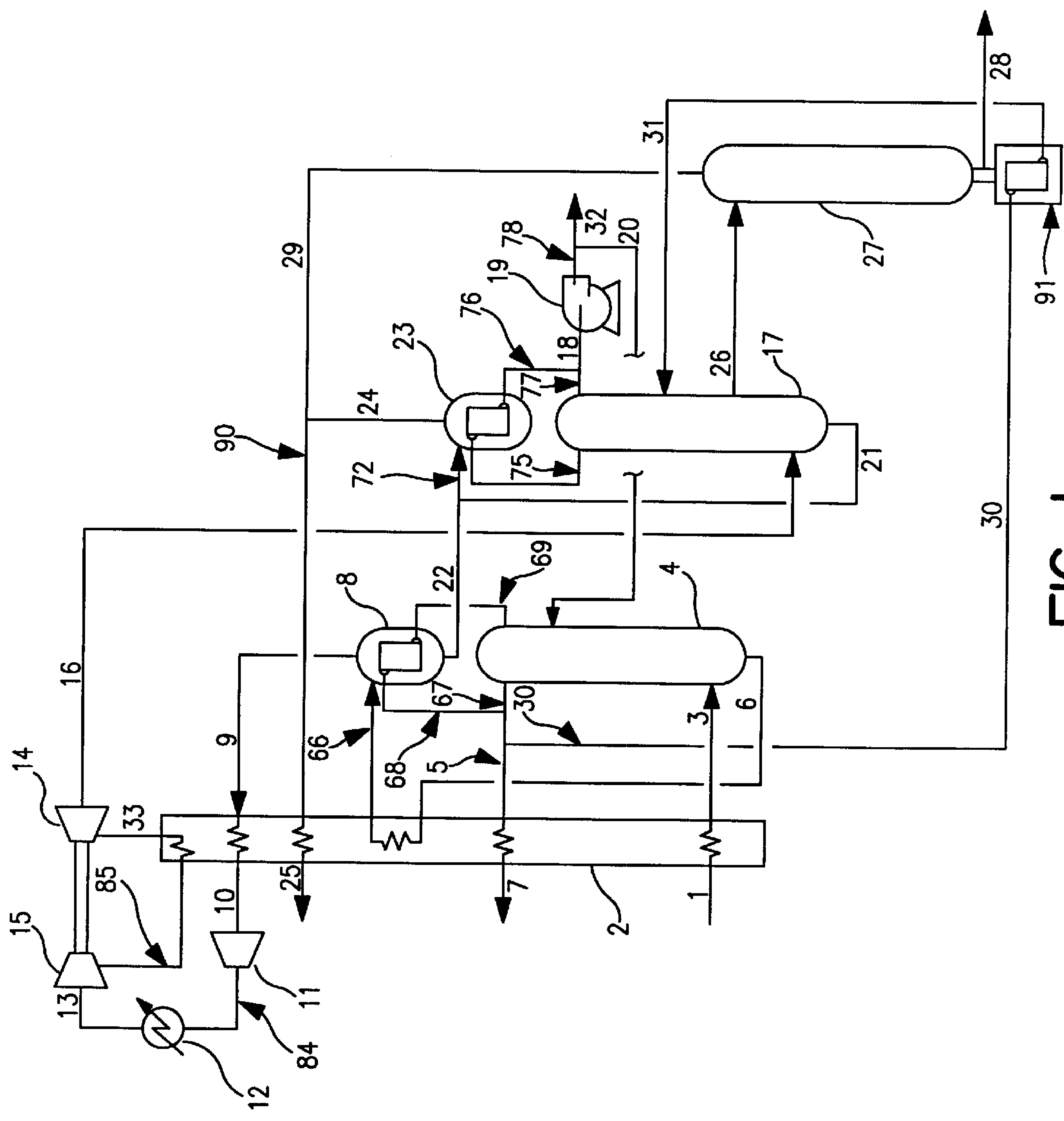

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FIG. 1

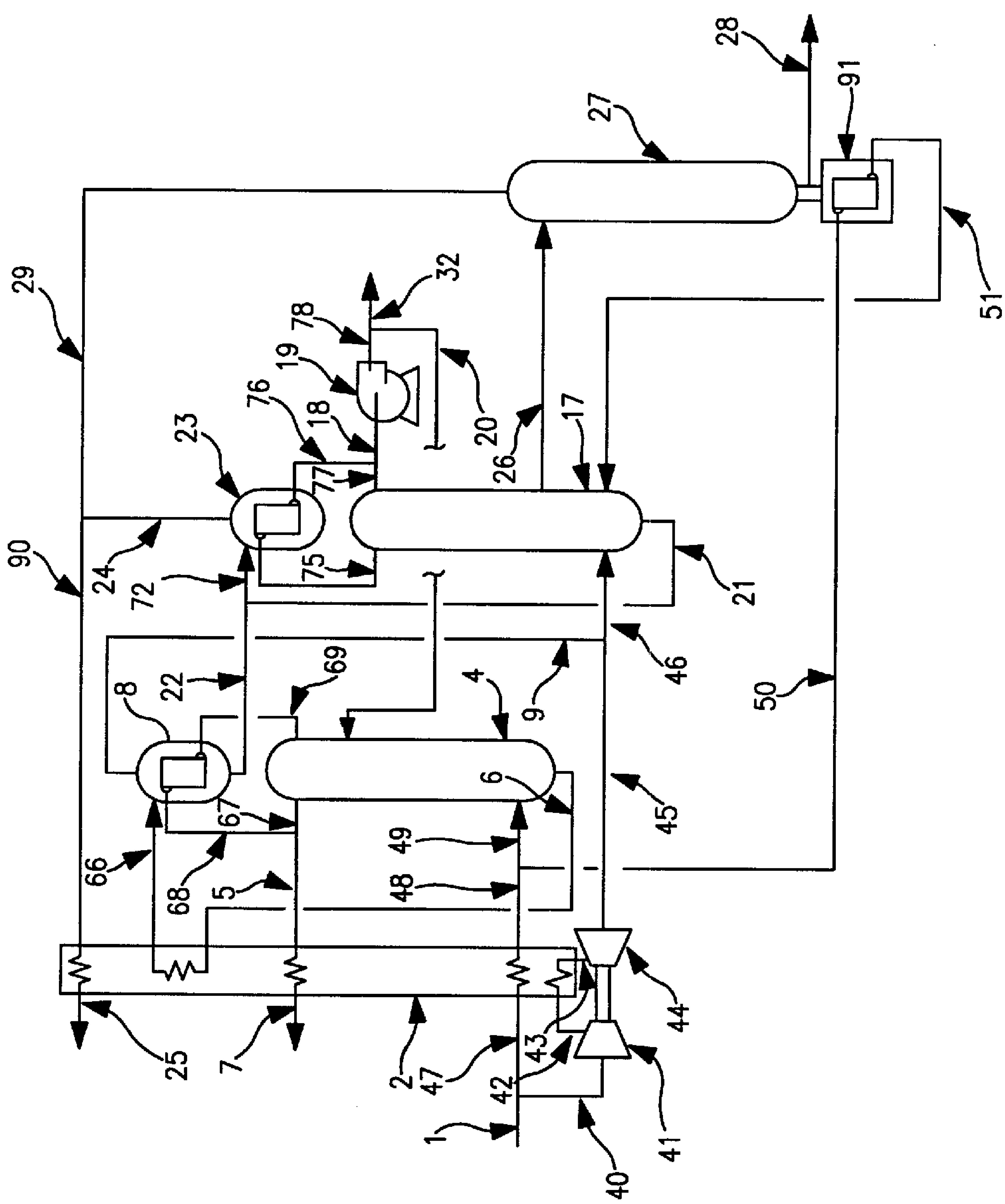
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FIG. 2

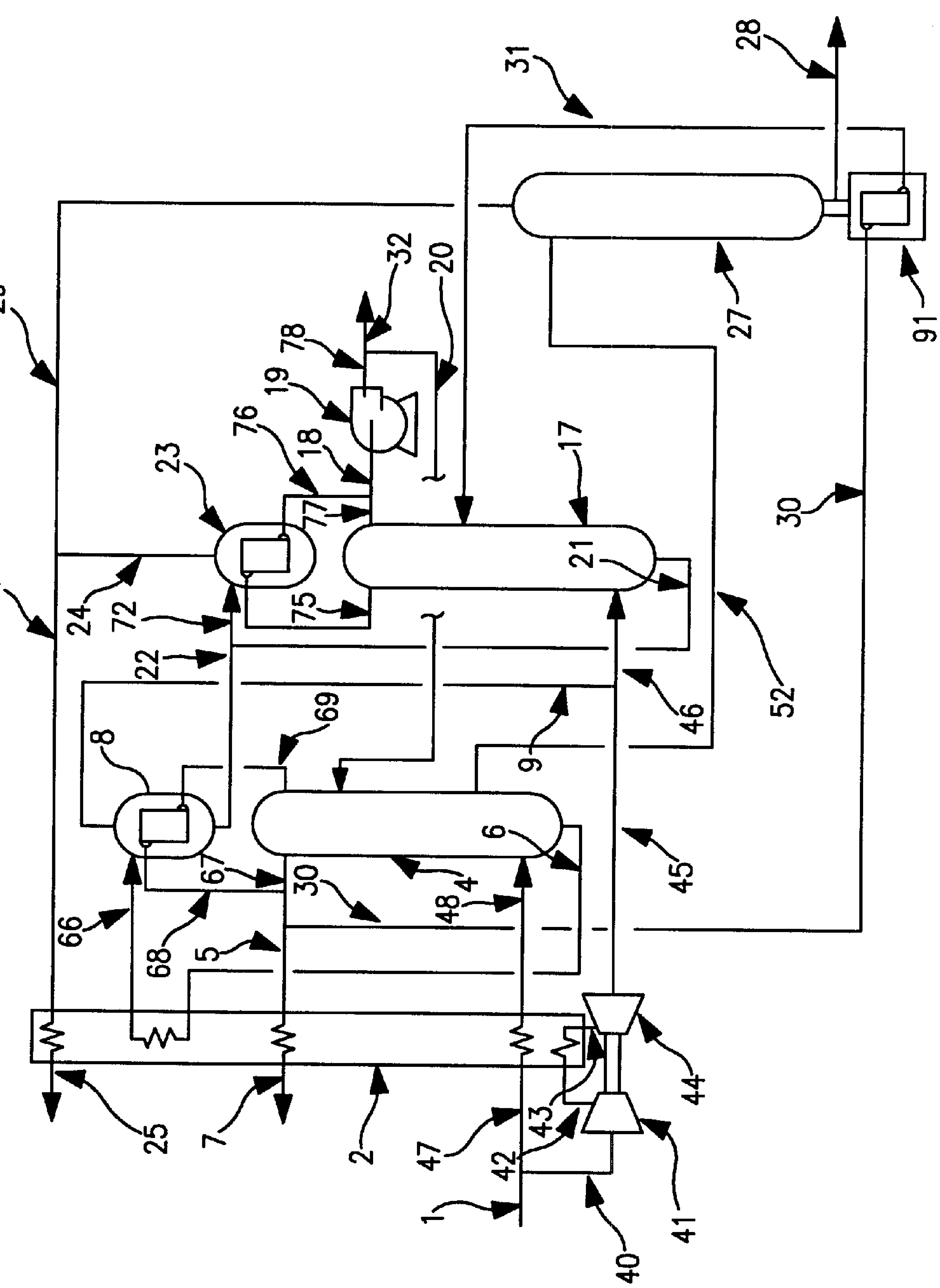
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FIG. 3

CRYOGENIC RECTIFICATION SYSTEM FOR PRODUCING HIGH PURITY OXYGEN

TECHNICAL FIELD

This invention relates generally to the cryogenic rectification of feed air and, more particularly, to the cryogenic rectification of feed air to produce high purity oxygen.

BACKGROUND ART

High purity oxygen is used in the manufacture of high value components such as semiconductors where freedom from contamination is critical to the manufacturing process. High purity oxygen is generally produced in large quantities by the cryogenic rectification of feed air using a double column plant. The production of high purity oxygen is energy intensive and any system which can produce high purity oxygen with lower power requirements than heretofore available systems would be highly desirable.

Accordingly it is an object of this invention to provide a system for producing high purity oxygen by the cryogenic rectification of feed air which has lower power requirements than do heretofore available comparable conventional systems.

SUMMARY OF THE INVENTION

The above and other objects, which will become apparent to those skilled in the art upon a reading of this disclosure, are attained by the present invention, one aspect of which is:

A method for producing high purity oxygen comprising:

(A) passing feed air at a feed level into a first column and producing by cryogenic rectification within the first column first nitrogen-rich fluid and first oxygen-enriched fluid;

(B) passing first oxygen-enriched fluid from the first column at a feed level into a second column having a top condenser, and producing by cryogenic rectification within the second column second nitrogen-rich fluid and second oxygen-enriched fluid;

(C) passing oxygen-containing liquid taken from above the feed level of at least one of the first column and the second column into the upper portion of a third column and down the third column countercurrently to upflowing vapor to produce high purity oxygen fluid;

(D) vaporizing a first portion of the high purity oxygen fluid by indirect heat exchange with at least one of feed air and first nitrogen-rich fluid to produce said upflowing vapor; and

(E) recovering a second portion of the high purity oxygen fluid as product high purity oxygen.

Another aspect of the invention is:

Apparatus for producing high purity oxygen comprising:

(A) a first column and means for passing feed air at a feed level into the first column;

(B) a second column having a top condenser and means for passing fluid from the lower portion of the first column at a feed level into the second column;

(C) a third column having a bottom reboiler and means for passing fluid taken from above the feed level of at least one of the first column and the second column into the upper portion of the third column;

(D) means for providing fluid from the lower portion of the third column to the bottom reboiler, and means for providing fluid from the upper portion of the first column to the bottom reboiler; and

(E) means for recovering high purity oxygen from the third column.

A further aspect of the invention is:

Apparatus for producing high purity oxygen comprising:

(A) a first column and means for passing feed air at a feed level into the first column;

(B) a second column and means for passing fluid from the lower portion of the first column at a feed level into the second column;

(C) a third column having a bottom reboiler and means for passing fluid taken from above the feed level of at least one of the first column and the second column into the upper portion of the third column;

(D) means for providing fluid from the lower portion of the third column to the bottom reboiler, and means for providing feed air to the bottom reboiler; and

(E) means for recovering high purity oxygen from the third column.

As used herein the term "feed air" means a mixture comprising primarily oxygen and nitrogen, such as ambient air.

As used herein the term "column" means a distillation or fractionation column or zone, i.e. a contacting column or zone, wherein liquid and vapor phases are countercurrently contacted to effect separation of a fluid mixture, as for example, by contacting of the vapor and liquid phases on a series of vertically spaced trays or plates mounted within the column and/or on packing elements such as structured or random packing. For a further discussion of distillation columns, see the Chemical Engineer's Handbook, fifth edition, edited by R. H. Perry and C. H. Chilton, McGraw-Hill Book Company, New York, Section 13, *The Continuous Distillation Process.*

Vapor and liquid contacting separation processes depend on the difference in vapor pressures for the components. The high vapor pressure (or more volatile or low boiling) component will tend to concentrate in the vapor phase whereas the low vapor pressure (or less volatile or high boiling) component will tend to concentrate in the liquid phase. Partial condensation is the separation process whereby cooling of a vapor mixture can be used to concentrate the volatile component(s) in the vapor phase and thereby the less volatile component(s) in the liquid phase. Rectification, or continuous distillation, is the separation process that combines successive partial vaporizations and condensations as obtained by a countercurrent treatment of the vapor and liquid phases. The countercurrent contacting of the vapor and liquid phases is generally adiabatic and can include integral (stagewise) or differential (continuous) contact between the phases. Separation process arrangements that utilize the principles of rectification to separate mixtures are often interchangeably termed rectification columns, distillation columns, or fractionation columns. Cryogenic rectification is a rectification process carried out at least in part at temperatures at or below 150 degrees Kelvin (K).

As used herein the term "indirect heat exchange" means the bringing of two fluids into heat exchange relation without any physical contact or intermixing of the fluids with each other.

As used herein the term "top condenser" means a heat exchange device that generates column downflow liquid from column vapor.

As used herein the term "bottom reboiler" means a heat exchange device that generates column upflow vapor from column liquid.

As used herein the terms "turboexpansion" and "turboexpander" mean respectively method and apparatus for the flow of high pressure gas through a turbine to reduce the pressure and the temperature of the gas thereby generating refrigeration.

As used herein the term "subcooling" means cooling a liquid to be at a temperature lower than the saturation temperature of that liquid for the existing pressure.

As used herein the terms "upper portion" and "lower portion" mean those sections of a column respectively above and below the mid point of the column.

As used herein the term "high purity oxygen" means a fluid having an oxygen concentration of at least 90 mole percent.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a simplified schematic representation of one particularly preferred embodiment of the cryogenic rectification system of this invention.

FIG. **2** is a simplified schematic representation of one preferred embodiment of the cryogenic rectification system of this invention.

FIG. **3** is a simplified schematic representation of another preferred embodiment of the cryogenic rectification system of this invention.

DETAILED DESCRIPTION

The invention will be described in detail with reference to the Drawings. Referring now to FIG. **1**, feed air **1**, which has been cleaned of high boiling impurities such as water vapor, carbon dioxide and hydrocarbons, and is at a pressure generally within the range of from 100 to 300 pounds per square inch absolute (psia), is cooled, preferably to about its dew point by indirect heat exchange with return streams by passage through main heat exchanger **2**. Cleaned cooled feed air emerging from main heat exchanger **2** is passed as stream **3** into the lower portion of first column **4**.

First column **4** is operating at a pressure generally within the range of from 100 to 300 psia. Within first column **4** the feed air is separated by cryogenic rectification into first nitrogen-rich fluid and first oxygen-enriched fluid. First oxygen-enriched fluid is withdrawn from the lower portion of first column **4** in liquid stream **6**, subcooled in main heat exchanger **2** and passed as stream **66** into the boiling side of first column top condenser **8**. First column top condenser **8** could be a single stage unit as illustrated in FIG. **1** or could contain one or more rectification stages above the condensing side of the unit.

First nitrogen-rich fluid is withdrawn as vapor stream **67** from the upper portion of first column **4**. A first portion **5** of stream **67** is warmed by passage through primary heat exchanger **2** and may be recovered as product nitrogen gas **7** having a nitrogen concentration generally of at least 99 mole percent. A second portion **68** of the first nitrogen-rich vapor is passed into the condensing side of first column top condenser **8** wherein it is condensed by indirect heat exchange with the first oxygen-enriched fluid. The resulting condensed nitrogen-rich liquid is passed in stream **69** from first column top condenser **8** into the upper portion of first column **4** as reflux. A third portion **30** of the nitrogen-rich vapor is used to drive the third column reboiler as will be more fully described below.

First oxygen-enriched liquid **66** is at least partially vaporized by the aforesaid indirect heat exchange with the first nitrogen-rich vapor in first column top condenser **8**. The resulting first oxygen-enriched vapor **9** from first column top condenser **8**, which typically has an oxygen concentration within the range of from 25 to 50 mole percent, is turboexpanded to generate refrigeration and this refrigeration is used to drive the rectification. The embodiment of the invention illustrated in FIG. **1** is a preferred embodiment wherein the first oxygen-enriched vapor from top condenser **8** is compressed prior to the turboexpansion.

Referring back now to FIG. **1**, first oxygen-enriched vapor **9** is warmed in main heat exchanger **2** to form oxygen-enriched vapor stream **10**. Stream **10** is compressed by passage through compressor **11** and resulting compressed stream **84** is cooled of the heat of compression in cooler **12** to form stream **13**. Oxygen-enriched vapor stream **13** is compressed, generally to a pressure within the range of from 50 to 350 psia, by passage through compressor **15** and compressed oxygen-enriched vapor stream **85** from compressor **15** is cooled by partial traverse through main heat exchanger **2**, and resulting cooled compressed oxygen-enriched vapor stream **33** is passed to turboexpander **14** wherein it is turboexpanded to generate refrigeration.

The embodiment of the invention illustrated in FIG. **1** is a particularly preferred embodiment wherein turboexpander **14** is mechanically coupled to compressor **15** thereby serving to drive compressor **15**. Refrigeration bearing oxygen-enriched vapor stream **16** from turboexpander **14** is passed into the lower portion of second column **17**.

Second column **17** is operating at a pressure generally within the range of from 40 to 150 psia. It is an important aspect of this invention that the first column and the second column do not share a common condenser/reboiler. Within second column **17** the first oxygen-enriched fluid is separated by cryogenic rectification into second nitrogen-rich fluid and into second oxygen-enriched fluid. The second oxygen-enriched fluid is withdrawn from the lower portion of second column **17** as liquid stream **21** and passed into the boiling side of second column top condenser **23**. In the case where the first oxygen-enriched fluid is not completely vaporized in first column top condenser **8**, the remaining liquid may be passed from the first column top condenser into the boiling side of the second column top condenser. This procedure is illustrated in FIG. **1** wherein remaining oxygen-enriched liquid is withdrawn from first column top condenser **8** in stream **22**, combined with stream **21** to form stream **72**, and passed into the boiling side of second column top condenser **23**.

Second nitrogen-rich fluid is withdrawn as vapor stream **75** from the upper portion of second column **17** and passed into the condensing side of second column top condenser **23** wherein it is condensed by indirect heat exchange with the fluids which were passed into the boiling side of second column top condenser **23**. The resulting boil-off vapor is withdrawn from second column top condenser **23** in second oxygen-enriched vapor stream **24**. Condensed second nitrogen-rich liquid is withdrawn from second column top condenser **23** in stream **76** and a first portion thereof is passed as stream **77** into the upper portion of second column **17** as reflux. A second portion **18** of second nitrogen-rich liquid **76** is pumped through liquid pump **19** to form pumped nitrogen-rich liquid stream **78**. If desired, a portion **32** of stream **78** may be recovered as liquid nitrogen product having a nitrogen concentration generally of at least **99** mole percent. The remainder **20** of stream **78** is passed into the upper portion of first column **4** as additional reflux. Second oxygen-enriched vapor **24** from second column top condenser **23** is warmed by passage through main heat exchanger **2** and removed from the system as stream **25**, preferably, as shown in FIG. **1**, in combination with top vapor from the third column.

Oxygen-containing liquid, generally having an oxygen concentration within the range of from 5 to 40 mole percent, is withdrawn from second column **17** and passed in stream **26** in the upper portion of third or stripping column **27** which is operating at a pressure generally within the range of from 14.7 to 150 psia. The oxygen-containing liquid is taken from second column **17** at a level which is above the feed level where the first oxygen-enriched fluid is passed into second column **17**. Generally the withdrawal level of stream **26** will be from 1 to 20 equilibrium stages above the feed level of stream **16**.

The oxygen-containing liquid passed into third column **27** flows down third column **27** against upflowing vapor and in the process lighter components within the downflowing liquid, e.g. argon, are passed into the upflowing vapor while oxygen in the upflowing vapor is passed into the downflowing liquid. This results in the production of high purity oxygen at the bottom of third column **27** and a waste fluid at the top of third column **27**. Waste fluid is withdrawn from the upper portion of third column **27** as stream **29** and passed out of the system. Preferably, as illustrated in FIG. **1**, stream **29** is combined with stream **24** to form stream **90** which is then warmed by passage through main heat exchanger **2** and removed from the system as aforesaid stream **25**.

High purity oxygen liquid is passed into the boiling side of third column bottom reboiler **91** wherein it is reboiled to generate the upflowing vapor used in third column **27**. A portion of the high purity oxygen fluid is recovered as product high purity oxygen as shown by product stream **28**. The product high purity oxygen may be recovered as liquid before the reboil in reboiler **91**, or as vapor after the reboil in reboiler **91**, or as both liquid and vapor. First nitrogen-rich vapor in stream **30** is passed into the condensing side of reboiler **91** wherein it condenses thereby serving by indirect heat exchange to vaporize high purity oxygen liquid passed into reboiler **91**. Resulting first nitrogen-rich liquid is passed from reboiler **91** in stream **31** into second column **17** wherein it serves as additional input to produce the second nitrogen-rich fluid and second oxygen-enriched fluid.

FIG. **2** illustrates another embodiment of the invention. The numerals of FIG. **2** are the same as those of FIG. **1** for the common elements and these common elements will not be described again in detail.

Referring now to FIG. **2**, first oxygen-enriched vapor **9** from first column top condenser **8** is not turboexpanded as in the embodiment illustrated in FIG. **1** but rather is passed directly from first column top condenser **8** into the lower portion of second column **17**. In the embodiment illustrated in FIG. **2**, a portion **40** of feed air **1** is further compressed by passage through compressor **41** to a pressure generally within the range of from 100 to 350 psia, resulting in a further compressed feed air stream **42** which is cooled by partial traverse of main heat exchanger **2**. Resulting cooled feed air stream **43** is turboexpanded by passage through turboexpander **44** to generate refrigeration and resulting refrigeration bearing feed air stream **45** is passed into the lower portion of second column **17** as feed. Preferably, as shown in FIG. **2**, stream **45** is combined with stream **9** to form feed stream **46** for passage into the lower portion of second column **17**.

A second portion **47** of feed air **1** is cooled by passage through main heat exchanger **2**, emerging therefrom as cleaned cooled feed air stream **48**. A portion **49** of stream **48** is passed into first column **4** as feed for this column. Another portion **50** of the cleaned cooled feed air from the main heat exchanger is passed into the condensing side of reboiler **91** wherein it is at least partially condensed to vaporize by indirect heat exchange high purity oxygen liquid. The resulting at least partially condensed feed air stream **51** from reboiler **91** is passed into the lower portion of second column **17** as additional input to produce the second nitrogen-rich fluid and second oxygen-enriched fluid.

FIG. **3** illustrates another embodiment of the invention. The numerals of FIG. **3** correspond to those of FIGS. **1** and **2** for the common elements and these common elements will not be described again in detail.

Referring now to FIG. **3**, the oxygen-containing liquid fed into third column **27** is not taken from second column **17** as was the case with the embodiments illustrated in FIGS. **1** and **2**. In the embodiment of the invention illustrated in FIG. **3**, oxygen-containing liquid, generally having an oxygen concentration within the range of from 5 to 40 mole percent, is withdrawn from first column **4** and passed in stream **52** into the upper portion of third column **27**. The oxygen-containing liquid in stream **52** is taken from first column **4** at a level which is above the feed level where the feed air is passed into first column **4**. Generally the withdrawal level of stream **52** will be from 1 to 20 equilibrium stages above the feed level of feed air stream **48** of the embodiment illustrated in FIG. **3**.

To illustrate the advantages of the invention over known systems, there is presented in Table 1 a comparison of the power requirements of one example the invention carried out in accordance with the embodiment illustrated in FIG. **1**, reported in column A and one example of the invention carried out in accordance with the embodiment illustrated in FIG. **2**, reported in column B, with the power requirements of an example of a comparable known process reported in column C. The known process is that disclosed in U.S. Pat. No. 5,918,482. As can be seen from the data reported in Table 1, the system which employs first nitrogen-rich fluid to drive the third column reboiler enables in this example a better than 9 percent power advantage over the known system, and the system which employs feed air to drive the third column reboiler enables in this example a better than 7 percent power advantage over the known system.

TABLE 1

	A	B	C
Air Flow (cfh-NTP)	241,000	247,000	238,500
Air Pressure (psia)	144.1	143.7	176.8
Gaseous Nitrogen Flow (cfh-NTP)	110,000	110,000	110,000
Liquid Nitrogen Flow (cfh-NTP)	1,100	1,100	1,100
Nitrogen Purity (ppb O_2)	0.3	0.3	0.3
Nitrogen Pressure (psia)	134.7	134.7	134.7
Liquid Oxygen Flow (cfh-NTP)	2,200	2,200	2,200
Oxygen Hydrocarbon Content (ppb)	0.1	0.1	0.1
Oxygen Argon Content (ppb)	1.8	1.8	1.8
Power (kw)	773.0	790.0	855.8

Although the invention has been described in detail with reference to certain preferred embodiments, those skilled in the art will recognize that there are other embodiments of the invention within the spirit and the scope of the claims.

What is claimed is:

1. A method for producing high purity oxygen comprising:

(A) passing feed air at a feed level into a first column and producing by cryogenic rectification within the first column first nitrogen-rich fluid and first oxygen-enriched fluid;

(B) passing first oxygen-enriched fluid from the first column at a feed level into a second column having a top condenser, and producing by cryogenic rectification within the second column second nitrogen-rich fluid and second oxygen-enriched fluid;

(C) passing oxygen-containing liquid taken from above the feed level of at least one of the first column and the second column into the upper portion of a third column and down the third column countercurrently to upflowing vapor to produce high purity oxygen fluid;

(D) vaporizing a first portion of the high purity oxygen fluid by indirect heat exchange with at least one of feed air and first nitrogen-rich fluid to produce said upflowing vapor; and

(E) recovering a second portion of the high purity oxygen fluid as product high purity oxygen.

2. The method of claim **1** wherein the first oxygen-enriched fluid is turboexpanded prior to being passed into the second column.

3. The method of claim **1** wherein the oxygen-containing liquid passed into the third column is taken from the first column.

4. The method of claim **1** wherein the oxygen-containing liquid passed into the third column is taken from the second column.

5. The method of claim **1** wherein the first portion of the high purity oxygen fluid is vaporized by indirect heat exchange with feed air.

6. The method of claim **1** wherein the first portion of the high purity oxygen fluid is vaporized by indirect heat exchange with first nitrogen-rich fluid.

7. The method of claim **1** further comprising turboexpanding a feed air stream and passing the turboexpanded feed air into the second column.

8. Apparatus for producing high purity oxygen comprising:

(A) a first column and means for passing feed air at a feed level into the first column;

(B) a second column having a top condenser and means for passing fluid from the lower portion of the first column at a feed level into the second column;

(C) a third column having a bottom reboiler and means for passing fluid taken from above the feed level of at least one of the first column and the second column into the upper portion of the third column;

(D) means for providing fluid from the lower portion of the third column to the bottom reboiler, and means for providing fluid from the upper portion of the first column to the bottom reboiler; and

(E) means for recovering high purity oxygen from the third column.

9. The apparatus of claim **8** further comprising a turboexpander wherein the means for passing fluid from the lower portion of the first column at a feed level into the second column includes the turboexpander.

10. The apparatus of claim **8** comprising means for passing fluid taken from above the feed level of the first column into the upper portion of the third column.

11. The apparatus of claim **8** comprising means for passing fluid taken from above the feed level of the second column into the upper portion of the third column.

12. The apparatus of claim **8** further comprising means for recovering product nitrogen from at least one of the upper portion of the first column and the upper portion of the second column.

13. The apparatus of claim **8** further comprising means for passing feed air into the second column, said means comprising a turboexpander.

14. Apparatus for producing high purity oxygen comprising:

(A) a first column and means for passing feed air at a feed level into the first column;

(B) a second column and means for passing fluid from the lower portion of the first column at a feed level into the second column;

(C) a third column having a bottom reboiler and means for passing fluid taken from above the feed level of at least one of the first column and the second column into the upper portion of the third column;

(D) means for providing fluid from the lower portion of the third column to the bottom reboiler, and means for providing feed air to the bottom reboiler; and

(E) means for recovering high purity oxygen from the third column.

15. The apparatus of claim **14** further comprising a turboexpander wherein the means for passing fluid from the lower portion of the first column at a feed level into the second column includes the turboexpander.

16. The apparatus of claim **14** comprising means for passing fluid taken from above the feed level of the first column into the upper portion of the third column.

17. The apparatus of claim **14** comprising means for passing fluid taken from above the feed level of the second column into the upper portion of the third column.

18. The apparatus of claim **14** further comprising means for recovering product nitrogen from at least one of the upper portion of the first column and the upper portion of the second column.

19. The apparatus of claim **14** further comprising means for passing feed air into the second column, said means comprising a turboexpander.

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